Crystal and molecular structure of tris(2,6-dichlorophenyl) thiophosphate

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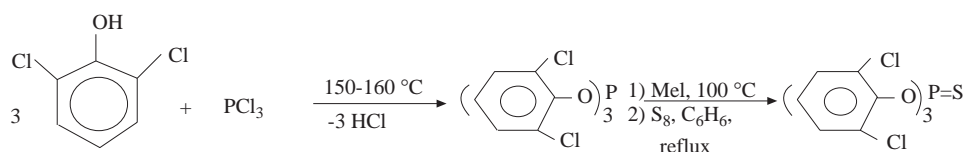*Meston Walk, Aberdeen, AB9 2UE, UK*

The crystal structure of tris(2,6-dichlorophenyl)thiophosphate was determined by single crystal X-ray diffractometry. The structure consists of isolated molecules and each unit cell contains 8 molecules of the compound. The crystal system is monoclinic with a space group of C2/c. The P atom is bonded to three O atoms and one S atom in a distorted tetrahedron environment.

Introduction

Phosphorus compounds are used in the plastics industry, food manufacture, water treatment, and also as insecticides, detergent and oil additivites[1]. In the course of studying sulfur-containing organo-phosphorus compounds, Odabaşoğlu and Gümrükçüoğlu synthesized some novel arylthiophosphates and arylphoshoro-thiochloridates[2]. Single crystal X-ray analyses of some of these crystalline componds were studied by Odabaşoğlu et al.[3] and Büyükgüngör et al[4]. In this paper, we report the molecular and crystal structure of tris(2,6,dichlorophenyl)thiophosphate from the same family.

Experimental

The compound was synthesized using a method described by Kamai and Bogdanov[5]. 0.15 mol PCl_3 and 0.1 mol 2,6-dichlorophenol were mixed and stirred in an oil bath at $150°C$ for 2 hours. After the removal of the excess PCl_3, the synthesized product, tris 2,6-dichlorophenyl phosphite, was purified by vacum distillation. An equivalent amount of methyl iodide was mixed with tris 2,6-dichlorophenyl phosphite in a sealed glass tube and heated to $100°C$. The reaction product was reacted with S_8 and refluxed in C_6H_6 for 12 hours. The synthesis reaction is formulated below:

Scheme 1.

Crystal and molecular structure of tris(2,6-dichlorophenyl) thiophosphate *V.T. YILMAZ et.al.,*

In order to obtain crystals suitable for X-ray analysis, the compound was recrystallized from a mixture of n-hexane and dioxane (1:1).

Single crystal X-ray diffraction data were obtained from a colourless crystal on a Nicolet P3 four-circle diffractometer with MoK_α radiation and graphite monochromator at 298 K. The cell parameters were determined using 14 reflections in the θ range of 7.5-11.4. Data collection used ω scan rates of 1.0 (Ip<150) to 29.3 (Ip>2500)° min^{-1} where Ip was the prescan intensity. The scan width was $0.6°\omega$. Background counts were taken at $\mp 1.0°$ in ω from the Bragg angle of each reflection. Atomic scattering factors were taken from the Int. Tables for X-ray crystallography[6]. The RDNIC program[7] was used for data reductions and SHELXS86[8] and SHELX76[9] were used for the structure solution and refinement, respectively. Further detail concerning data collection and refinement are given in Table 1. All non-H atoms were refined anisotropically. H atoms were placed in calculated positions with C-H=0.95Å. The molecular diagram was obtained using the ORTEX graphics program[10]. All computations were performed on the SUN SPARCServer (UNIX operating system) of the computing centre of University of Aberdeen.

Table 1. Crystallographic data and refinement parameters for tris(2,6-dichlorophenyl)thiophoshate

Formula	$C_{18}H_{19}Cl_6O_3PS$	Temperature (K)	298
Mw	549.03	Radiation, $\lambda(\overset{\circ}{A})$	MoK_α0.71073
crystal size(mm)	0.5×0.4×0.4	Range of hkl	$\mp$33; 0-9;0-22
Crystal colour	Colourless	Scan type	ω
Crystal system	Monoclinic	$2\theta_{max}(\circ)$	25
Lattice parameters		Standard reflection	2
a(Å)	28.443(23)	Max. intensity variation(%)	4.4
b(Å)	8.283(7)	Internal	50
c(Å)	18.659(10)	No. of reflections measured	4187
$\alpha(\circ)$	90	No.of independent reflections	3116
$\beta(\circ)$	99.54	No. of observed reflections	2075
$\gamma(\circ)$	90	R	0.103
V(Å^3)	4335(5)	R_w	0.110
Space group	C2/c	S	1.341
Z	8	No. of reflections used	2075
D_C(gcm^{-1})	1.682	No. of reflect. paramtr. refined	263
Reflections for	lattice parameters	Weight scheme	$1/(\sigma^2F+0.000511F^2)$
Number	14	Max.A/σ	0.017
θ range ($\circ$)	7.5-11.4	Pmin-max (e Å^{-3})	-1.15
μ (cm^{-1})	0.98		

Results and Discussion

The shape of the molecule with the atomic numbering scheme is shown in Figure 1. The fractional atomic coordinates and equivalent isotropic displacement parameters for non-H atoms are given in Table 2. The selected bond angles and distances are listed in Table 3.

The structure of the compound is quite similar to those of sulfur-containing organo-phoshorus compounds reported in previous studies[3,4]. The asymmetric unit of the compound comprises one third of the formula unit. The P and S atoms are located on the threefold axis. The average values of the O-P-S and the O-P-O angles are 116.7(3)° and 101.3(3)°, respectively. These values are significantly different from

the ideal tetrahedral angle of 109.5°, but suggest a distorted tetrahedral geometry around the central P atom. Similar observations were reported for tris(2-isopropyl-5-methylphenyl)phosphate[3] and tris(o-4-ter-butylphenyl)-phosphate [4].

Table 2. Fractional atomic coordinates (x10^4) and equivalent isotropic displacement parameters ($\mathring{A}^2$, $\times$ 10^3) for non-hydrogen atoms with e.s.d. in parentheses.

$U_{eq} = (1/3) \sum i \sum j U_{ij} a * ia * jai.aj$

	x/a	y/b	z/c	U_{eq}
P	3695.8(10)	755(5)	3300.4(13)	68.7(13)
C/l	3398.0(15)	-3313(5)	3813.8(19)	115.3(18)
C/2	3037.2(12)	2678(5)	4647.6(17)	96.3(16)
C/3	2670.9(14)	3200(6)	2632(2)	121.3(18)
C/4	4555.7(17)	3924(8)	2954(4)	207(3)
C/5	4288.2(15)	3104(5)	4931(3)	142(2)
C/6	4744.8(19)	-1901(10)	3372(3)	220(3)
S	3728.4(14)	-72(5)	2370(2)	106.5(18)
O1	3246(2)	187(10)	3626(3)	70(2)
O2	3668(3)	2695(10)	3337(4)	71(3)
O3	4092(2)	335(8)	3982(3)	54(2)
C1	3215(4)	-354(19)	4311(5)	65(4)
C2	3253(4)	-1967(19)	4460(6)	74(5)
C3	3189(4)	-2623(19)	5128(7)	86(5)
C4	3078(5)	-1604(23)	5637(7)	95(6)
C5	3.34(4)	36(24)	5519(6)	92(6)
C6	3096(4)	624(18)	4845(6)	75(5)
C7	3607(5)	3689(16)	2725(6)	78(5)
C8	3161(5)	4030(18)	2383(6)	91(5)
C9	3117(8)	5167(21)	1793(8)	121(8)
C10	3511(10)	5839(27)	1605(10)	155(14)
C11	3938(8)	5439(23)	1921(10)	149(11)
C12	4000(6)	4349(19)	2510(7)	110(6)
C13	4557(4)	766(20)	4098(6)	80(5)
C14	4700(4)	2086(16)	4533(9)	95(6)
C15	5174(7)	2584(21)	4663(12)	151(10)
C16	5500(8)	1668(35)	4318(18)	196(17)
C17	5355(8)	407(39)	3940(14)	193(17)
C18	4900(5)	-108(23)	3808(8)	112(7)

The P=S double bond length of the compound is 1.884(4)Å, which is almost the same as that of tris(2-isoproply-5-methylphenyl)phosphate [1.886(4)Å][3], but smaller than that of tris(o-4-ter-butylphenyl)-phosphate[1.908(1)Å][4]. The mean P-O bond distance is 1.593(7)Å, which is also similar to the reported compounds [1.588(6)Å][3] and [1.579(2)Å][4] and agrees with that of the P-OH bonds of orthophosphoric acid [1.576Å][6].

The phenyl ring do not exhibit any unexpected geometrical features. However, as a result of the efect of both the aromatic ring and the Cl atom, the mean C-O single bond is 1.373(12)Å, which is somewhat

Crystal and molecular structure of tris(2,6-dichlorophenyl) thiophosphate *V.T. YILMAZ et.al.,*

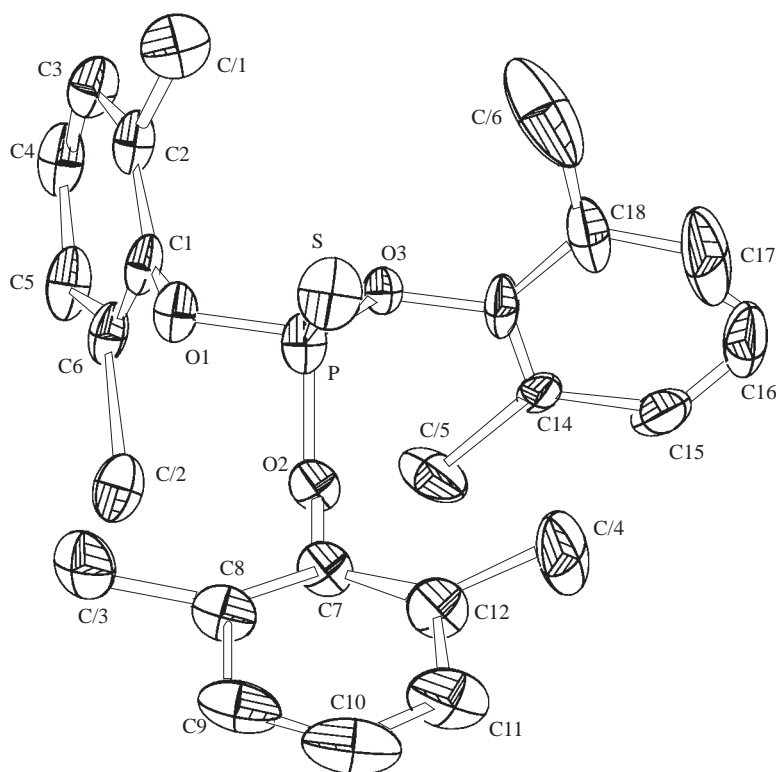shorter than a praffinic C-O bond of 1.43Å[6].

Figure 1. The molecule of tris(2,6-dichlorophenyl)thiophoshate showing atom labels and 20% probability ellipsoids.

Table 3. Selected geometric parameters

Bond distances (Å)			
S-P	1.884(4)	C1-O1	1.371(11)
O1-P	1.577(7)	C7-O2	1.395(12)
O2-P	1.611(9)	C13-O3	1.353(12)
O3-P	1.592(6)	C2-C1	1.466(17)
C2-Cll	1.740(13)	C6-C1	1.369(16)
C6-Cl2	1.743(14)	C3-C2	1.399(16)
C8-C13	1.688(15)	C4-C3	1.347(18)
C12-Cl4	1.695(16)	C5-C4	1.379(19)
C14-Cl5	1.710(16)	C6-C5	1.387(15)
C18-Cl6	1.715(19)		
Bond angles (∘)			
O1-P-S	114.4(3)	O3-P-O2	102.5(4)
O2-P-S	114.3(3)	C1-O1-P	129.6(6)
O3-P-S	121.4(3)	C7-O2-P	123.7(7)
O2-P-O1	103.4(4)	C13-O3-P	127.9(6)
O3-P-O1	98.0(3)		

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CONTENTS

CORRECTIONS

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Apocarbonic Anhydrase-Enzymatic Determination of Zinc in Fruit Juices Volume 21, Number 3, 165 (1997).

1. The following corrections is in order in Table 2: Z_n^{2+} concentration (μ g/100 g fruit)

2. in Figure 3: Absorbance values have to be multiplied by (0.1).